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Polymer-Attached Functional Inorganic-Organic Hybrid Nano-composite Aerogels

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ABSTRACT

Novel materials in which modified inorganic-organic hybrid silica aerogels are attached to polymer chains have been synthesized. The aerogels are based on chitosan, a bioderived polymer from chitin, and they contain silica. The first stage of the modifications includes attachment of isocyanate, amine onto the chitosan chains embedded within the aerogel. These groups are employed in the second stage to develop the reactions required to "string" aerogel particles along functionalized linear polymers or to employ these polymers to crosslink the composite aerogels. The initial chitosan-silica aerogel particles have an ultimate size of about 2nm, and their functionally modified forms were reacted at sizes up to 1 μm . These aerogels can take up and hold dyes and water-soluble drugs. The chemistry to synthesize polyamino-siloxane based aerogel composite was discussed. In addition, two approaches to synthesize PHEMA aerogel hybrid were studied.

INTRODUCTION

Chitosan silica aerogels in transparent or translucent monolithic solid form have been synthesized by an initial sol-gel process, followed by extraction with supercritical CO_2 [1-6]. The chitosan silica aerogels have high porosity, up to 95%(v/v), and densities ranging from 0.2 to 0.3g/cm³. The chitosan silica aerogels have average pore size of 3-5nm[2-3]. They have a three dimensional network which can be thought of as a Si-O-Si bonded framework with the chitosan polymer winding through the network like a snake that interacts with silica by both hydrogen bonds and Si-O-C bonds.

In recent work, we have demonstrated that the amine groups on the chitosan in the silica network are able to react with externally provided compounds. Thus, it is possible to carry out reactions on the chitosan molecule that is essentially suspended in the dry aerogel space. That makes it feasible to do chemical reactions where water must be excluded on a molecule (chitosan) that otherwise would only be available in solvents with active hydrogen [7]. Small molecules such as bis (4-isocyanatocyclohexyl) methane (HMDI), succinic anhydride (SA), isocyanatoethyl methacrylate (IEMA), and dansyl chloride (DC) have been used in this work to modify the chitosan in aerogel through chemical reactions with amines present in chitosan [7].

Of particular interest are the reaction of HMDI with chitosan silica aerogel, which results in a new -NCO terminated material, and, the reaction of IEMA with chitosan silica aerogel to produce a methacrylate terminated new aerogel material. They are valuable not only because they have new physical properties, but also because they bring new functional groups into these aerogels, making it possible to carry out new chemistries. This should lead to novel materials with varied properties.

One possibility is to attach these -NCO terminated aerogel particles in the 100nm to 1 μm size range to linear polymers such as poly (allyamine), aminopropylmethylsiloxane-dimethylsiloxane copolymer, or poly (2-hydroxyethyl methacrylate) (PHEMA).

The aminopropylmethylsiloxane-co-dimethylsiloxane copolymers are soluble in organic solvents that do not have active hydrogen, so it should be possible to carry out the reaction

between chitosan-silica aerogel particles with pendant -NCO-containing moieties, on one the hand, and amine groups on the substituted siloxane copolymer, on the other. However, poly (allyamine) and PHEMA are not very soluble in non-polar organic solvents that do not have active hydrogen atoms. Thus, reactions between pendant -NCO and -NH₂ or -OH groups, in which water has to be excluded, have been carried out in neat phases. Through such reactions, novel materials have been formed consisting of the polymer chain with aerogel attached, as shown conceptually in Figure 1.

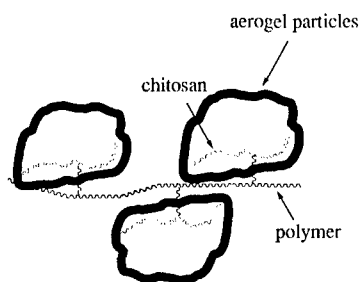


Figure.1 Schematically showing the structure of aerogel particles attached linear polymer.

By grinding monolithic chitosan-silica aerogel pieces, particles of aerogel can be obtained so that a functional group on a chitosan silica aerogel particle can react with a polymer molecule. It is useful to explore the reaction under concentration conditions that tend to favor a particle attached to a polymer molecule over these that favor a networks structure with chitosan silica aerogel particles serving as the crosslinking reagents. In this paper, we address the synthesis of two types of polymer-chitosan aerogel hybrid bonds. The first involves -NCO terminated aerogel reacting with aminopropylmethylsiloxane-dimethylsiloxane copolymer, and the second two methods are used to form chitosan aerogel PHEMA hybrids.

EXPERIMENTAL SECTION

1. Synthesis of isocyanate terminated chitosan-silica aerogel, X-SiO₂-NCO

The 10%(w/w) chitosan-silica aerogel was synthesized in our previous work [7]. The bulk pieces of these aerogel were ground into fine powder. The 0.176 g of the powder was combined with 0.360 g dicyclohexylmethane-4, 4' diisocyanate (HMDI, Bayer Corp.) in a 20 ml glass vial and 2ml THF was added to serve as solvent. After the mixture reacted for 3hrs at room temperature, the product was washed by THF for 6 times. For each time, 15 ml fresh THF was added and after 30 mins, the supernatant solvent was discarded. After it was washed, the product was dried in vacuum and its FT-IR spectrum was measured.

2. Reaction of X-SiO₂-NCO with amine pendant siloxane copolymer

A 0.06 g NCO-terminated aerogel was mixed with 0.6 g 4-5% aminopropylmethylsiloxane-dimethylsiloxane copolymer (AMS-152, Gelest, INC.) in a 20ml glass vial. After reacting for 40 minutes at room temperature, the mixture was washed by THF using the technique described above. Then the product was dried in vacuum and its FT-IR spectrum was measured. To make it clear that there is no interference from trace of water during the washing process, a blank sample of the isocyanate-terminated aerogel was washed the same way as a control.

The PHEMA polymer is an important polymer, which is widely used in biomedical applications due to its biocompatibility, high permeability and hydrophilicity. An aerogel attached PHEMA, could combine many of the valuable properties of this polymer and of chitosan-silica aerogel, and useful to investigate. It has been approached by combining the solid aerogel phase with solid polymers, and by two additional methods involving copolymerization of monomer 2-hydroxyethyl-methacrylate and methacrylate-terminated aerogel.

3. Reactions of X-SiO₂-NCO with HEMA monomers

First, 0.0366 g HMDI modified chitosan silica aerogel, X-SiO₂-NCO, calculated amount of 2-hydroxyethyl methacrylate (HEMA, Aldrich) monomer and dibutyltin dilaurate catalyst were mixed in a 20 ml glass vial. After it was heated at 67°C for 7 hrs, the mixture was washed by THF and then vacuum dried.

Second, 0.057 g HMDI modified chitosan silica aerogel, X-SiO₂-NCO, was mixed with calculated amount of HEMA and dibutyltin dilaurate catalyst. After it was heated at 67°C for 12 hrs, the mixture was washed by THF, and vacuum dried.

4. Synthesis of chitosan-silica aerogel pendant PHEMA hybrid composite by copolymerizing methacrylate terminated aerogel with HEMA monomer.

First, 0.2 g chitosan silica aerogel particles were mixed with 0.2 g isocyanatoethylmethacrylate (IEMA, Aldrich) in 5ml THF and reacted for 30 minutes at room temperature. The mixture was washed by THF and vacuum dried. A methacrylate-terminated aerogel was obtained. Second, 0.047 g this product was mixed with 0.57g HEMA monomers and 0.014g AIBN in 5 ml THF. The mixture was heated at 62°C for 30 minutes, then cooled down to room temperature for another 3 hours. Then the product was washed by THF and dried in vacuum. And its FT-IR spectrum was measured.

Infrared (FT-IR) spectra were measured on all samples using a Perkin Elmer 1600 spectrometer.

RESULTS AND DISCUSSION

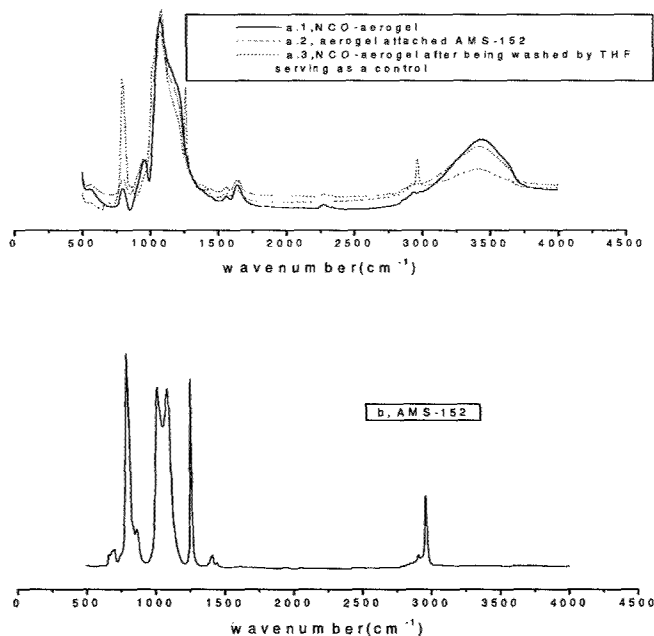


Figure 2, FT-IR spectra of (a.1) NCO-aerogel; (a.2) aerogel attached AMS-152; (a.3) NCO-aerogel after being washed by THF severing as a control of a.2; (b), AMS-

In the reaction of X-SiO₂ aerogel with HMDI, the amine groups on chitosan reacted with one isocyanate group of each HMDI. Thus, a urea linkage -NH-(C=O)-NH-, which has characteristic absorptions at 1660 cm⁻¹ and 1560 cm⁻¹, is formed at one end of each HMDI. However, on some of the HMDI molecules, one NCO is unreacted and available for further reaction [7]. This is shown in Figure 2.a.1, which has a peak at 2272 cm⁻¹, due to the stretching vibration of NCO.

This unreacted NCO group was utilized to react with amine groups that are on the amine pendant siloxane copolymer (AMS-152). The aerogel particles were attached to the siloxane polymer chain through urea linkage. In Figure 2.a.2, the disappearance of the peak for NCO at 2272 cm⁻¹ and the appearance of peak at 1262 cm⁻¹ (due to the symmetric CH₃ deformation vibration in Si-(CH₃)₂ from the silicone copolymer), the increased intensities at 800 cm⁻¹ (due to the symmetric Si-C stretching of Si-(CH₃)₂) and at 2963 cm⁻¹ (due to C-H) and the change in shape of the band in the range from 900 cm⁻¹ to 1200 cm⁻¹ due to addition of absorption bands at 1028 cm⁻¹ to 1102 cm⁻¹, all support this identification. Figure 2.a.3 shows that the NCO in the control product remained. This showed that water was not introduced during the THF washing process, which is effective in washing off the unreacted siloxane polymer.

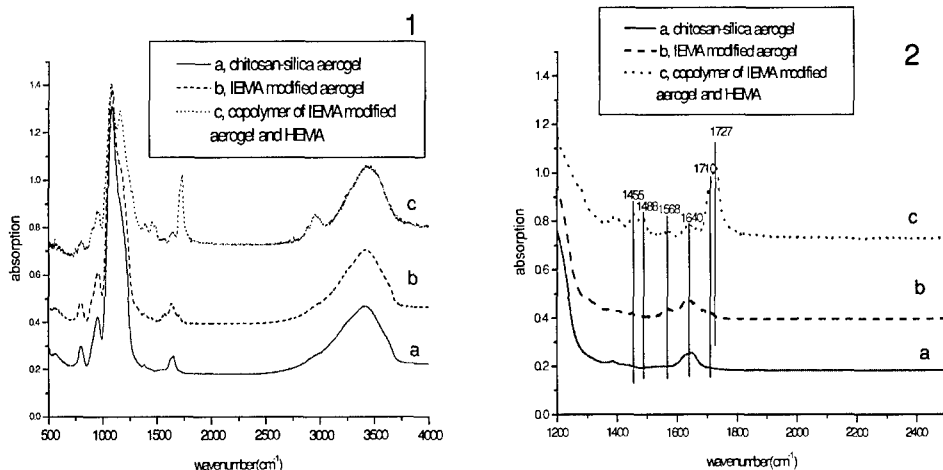


Figure 3, FT-IR spectra of (a), chitosan-silica-aerogel; (b), IEMA modified aerogel, the product after chitosan-silica-aerogel reacted with IEMA at room temperature for 30mins; (c), PHEMA aerogel hybrid, the product after (b) reacted with HEMA at 62°C for 30 minutes, then at room temperature for another 3 hours.

Reactions of IEMA with the chitosan-silica aerogel were successful. IEMA, which has an isocyanate group at one end and methacrylate group at the other end, was attached to chitosan within chitosan-silica-aerogel by forming a urea linkage between the isocyanate group and the amine on chitosan. Thus, the methacrylate group was attached and available for further chemistry. In Figure 3, spectrum b has peaks at 1568 cm^{-1} and 1710 cm^{-1} which spectrum a does not have. The peak at 1568 cm^{-1} is due to the combination of the bending of N-H and the stretching of C-N in the newly formed urea linkage. The urea linkage also has a characteristic peak at 1660 cm^{-1} due to $-(\text{C}=\text{O})-\text{N}-$, but it is merged into the strong O-H bending vibration of H_2O at 1630 cm^{-1} [3]. The stretching of $-\text{C}=\text{C}$ also contributes to the band at 1640 cm^{-1} . The peak at 1710 cm^{-1} on spectrum b is due to the $-\text{O}-\text{C}(\text{O})-\text{C}=\text{C}$ in the methacrylate group [7]. The resultant methacrylate terminated aerogel was copolymerized with monomer HEMA. In a certain circumstance, such as the right size of the aerogel particles and the right temperature, methacrylate terminated aerogel acted as a difunctional monomer, copolymerizing with monomer HEMA, and forming a linear hybrid, which contained a long chain with aerogel particles pendant along it. In Figure 3, new peaks at 1727 cm^{-1} , 1488 cm^{-1} and 1455 cm^{-1} appear in spectrum c. The strong peak at 1727 cm^{-1} is shifted from 1710 cm^{-1} , due to formation of $-\text{O}-\text{C}(\text{O})-\text{C}-\text{C}-$ from polymerization of $-\text{O}-\text{C}(\text{O})-\text{C}=\text{C}$ groups. Peaks at 1488 cm^{-1} and 1455 cm^{-1} are due to vibration of C-H of the PHEMA formed.

The HMDI modified chitosan-silica-aerogel was used to react with HEMA at ca. 60°C . The -NCO group reacts with the -OH of HEMA to form urethane linkages. As shown in Figure 4, the

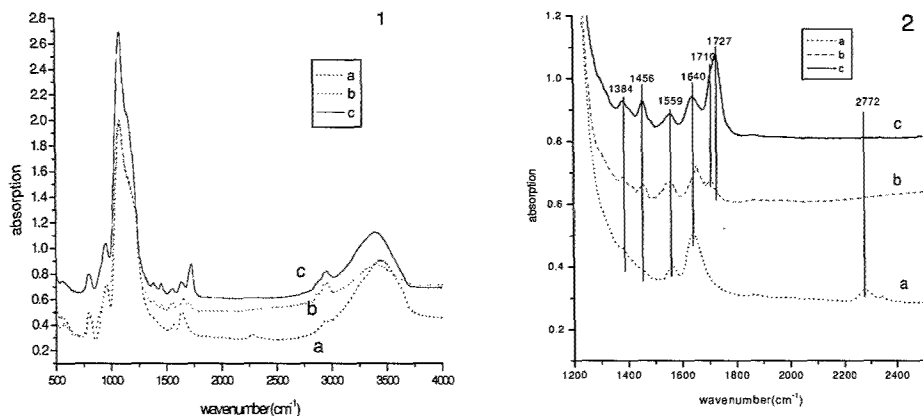


Figure 4, FT-IR spectra of (a), NCO-aerogel ($\text{X-SiO}_2\text{-NCO}$, the product of reaction of chitosan silica aerogel with HMDI); (b), HEMA terminated aerogel (the product of the reaction of NCO-aerogel with HEMA at 67°C for 7 hrs); (c), aerogel-PHEMA hybrid (the product of the reaction of NCO-aerogel with HEMA at 67°C for 12 hrs).

band at 2272 cm^{-1} due to NCO in spectrum a, is absent in spectrum b, and in b the 1559 cm^{-1} band is increased in relative intensity due to formation of the urethane linkage. Both the unpolymerized methacrylate group from HEMA and the formed urethane linkage contribute to the band at 1710 cm^{-1} . Thus, after heating the mixture of NCO terminated aerogel and HEMA at 67°C for 7 hours, HEMA molecules attached the aerogel by urethane linkage formed between hydroxyl groups on HEMA and NCO groups of the modified aerogel. This treatment caused addition but not much polymerization, as shown by the relatively weak peak at 1727 cm^{-1} for the $-\text{O}-\text{C}(=\text{O})-\text{C}-\text{C}$ groups. However, when the heating time is increased to 12 hours, the peak at 1727 cm^{-1} in spectrum c became stronger, meaning that the HEMA terminated aerogel copolymerized with HEMA monomers, and formed an aerogel PHEMA hybrid material. The shoulder at 1710 cm^{-1} showed that there were still some methacrylate groups left unreacted within the hybrid.

CONCLUSION

This study has shown that the small molecule modified chitosan-silica-aerogels, especially NCO-terminated and methacrylate terminated aerogels can be used either to combine with functional polymers or combine with other functional monomers to produce copolymers. Materials that contain polymer chains with aerogel particles attached to them have been prepared and could be quite interesting, because they combine the properties of the polymer and of the chitosan-silica aerogel. This work has shown that this kind of hybrid materials can be produced chemically. Future work will relate to investigation of the physical properties of these new materials.

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